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The invention describes the use from thermostable and plasma-corrode-stable polymers to the production of nano-structures in thin layer by Nanoimprintlithographie.

State of the art and disadvantages of the state of the art

Nano-structures on polymere-coated substrate materials become at present prepared by means of the electron, X-raying and ion beam lithography. By action of high-energy radiation on a polymer film made depending upon polymer structure a degradation or a crosslinking of the polymer in the irradiated ranges. The change of the solubility possible with a subsequent treatment in suitable solvents, achieved thereby, and/or. Solvent mixtures the development of the irradiated nano-structures and in a subsequent etching step the transmission of the structures into the substrate material. This technique is very time-consuming and cost-intensive, particularly if corresponding structures in large quantity and for the mass production of microelectronic devices made to become wide to be supposed. The optical lithography arrives during this pattern definition at its boundaries. Similar one was this so far with the already for a long time known embossing technology, became prepared with which first only coarse structures and the most diverse mouldings. Today the production of microstructures belongs by coining/shaping to the state of the art. Examples are the manufacture of Compact disks by structure coining of 1 μ m-structures in polycarbonates and the generation of 10 μ m-structures in PMMA or polyesters to the production of micromechanical components ((M. Harmening, W. Bacher, P. Bley, A. El-Kholi, H. Calf, B. Kowanz, W. Menz, A. Michel, J. Mohr, Proceedings IEEE Micro Electro Mechanical of system, 202 (1992) and H. Left, S. D. Senturia, Proceedings OF the 13 th IEEE/CHMT international electronics Manufacturing Technology symposium, 145 (1992)). Only 1998 are raised in US patent specification 5772905 the patentrechtliche claim, by coining/shaping also a pattern definition < to reach 25 Nm. For coining/shaping structures within the nanometer range in this patent the term is > > Nanoimprintlithographie< < used. Numerous publications predict that with the Nanoimprintlithographie in the near future also an industrial mass production will take place from nano-structures extremely inexpensive. For the Nanoimprintlithographie however embossing temperatures are required, which are appropriate for 80-120 DEG C over the glass transition temperature of the polymer. This is from major disadvantage, if it concerns to produce thermostable nano-structures how they become required for many applications in the optics, optoelectronics and microelectronics. Because with the use of polymers with a glass transition temperature of z. B. > 150 DEG C in the Nanoimprintlithographie would be embossing temperatures necessary, at which the decomposition of the polymers already begins. Predominant one became therefore for embossing attempts so far polymethyl methacrylate (PMMA) used. PMMA possesses a glass transition temperature of 105 DEG C, so that the most favorable temperatures for the generation of nano-structures are by coining/shaping about 200 DEG C. PMMA nano-structures possesses however for many applications a too small thermal stability and an insufficient plasma corroding stability.

The Mold lithographymethod (J. offers a way out. Haisma, M. Verheijen, K. of the Heuvel, J. of the mountain, J. Vacuum Science Technol. 14 (6). (1996) 4124-4128), with which also structures into the nanometer range prepared to become to be able. With this method photo-reactive monomers come in thin layer to the use. A corresponding structured stamp from quartz becomes with low pressure with the layer in contact brought and the monomer subsequent by UV exposure by the stamp crosslinked. The structure formation made here with low temperatures. In addition, the method shows major drawbacks. Problematic ones are the high volume contraction during coining/shaping, the partial adhesion of the polymer at the stamp or the detachment of the substrate as well as the necessary thermal post treatment, which are necessary to the stabilization of the generated structures. While with the Nanoimprintlithographie thermoplastic, particular polymethyl methacrylate, to the use come, methods cross-linkingable monomers used with Mold lithography, which lead to thermosetting polymers, become.

Object of the invention

The instant invention is the basis the object to eliminate disadvantage, which exist with the Nanoimprintlithographie, by the use from thermostable, drying-corrode-stable polymers to without in addition embossing temperatures of > 200 DEG C required become.

Solution of the object and advantages of the invention

The object becomes according to invention dissolved by the fact that polymers with aromatic structure units become used. Aromatic structure units in the polymer lead general to a higher plasma corroding stability.

Surprising one is the effect that opposite aliphatic polymers in the case of a comparable glass transition temperature also an increase of the thermostability of the generated structures results. An other increase of the thermal stability can become achieved, if the polymers contain additional cross-linkingable allyl groups. The radical polymerization of allyl monomers leads due to of Kettenübertragungsreaktionen only to the formation of short polymerization chains, why with the polymerization of monofunctional Vinyl, methacrylat, and acrylate monomers presence of polyfunctional allyl monomers a crosslinking occurs only with an high monomer conversion. Thereby still reactive prepolymers isolated can become, which possess an excellent solubility in organic solvents and exhibit excellent layer education characteristics. A stepwise polymerization of monofunctional Vinyl, methacrylat, and acrylate monomers in presence of polyfunctional methacrylate, acrylate or vinyl monomers cannot be accomplished. Already with a very small monomer conversion here the point of gel becomes achieved, and an insulation of soluble prepolymers is not possible. With the copolymerization of polyfunctional allyl monomers in-polymerized portion of allyl monomer works as reactive softeners. The glass transition temperature becomes first lowered. This the possible flow during coining/shaping, before through reaction of the still present polymerizationable allyl groups the softener effect lost goes and crosslinked polymers with a higher glass transition temperature and thus increased a thermal stability formed become. A corresponding effect can be also obtained, if the polymers cross-linkingable polyfunctional allyl connections become added. These allyl monomers take over both with the copolymerization and with the doping the reactive softener function.

To the invention process in detail the subsequent is to be implemented:

For the application according to invention preferred aromatic and cyclo-aliphatic Homo comes and/or. Copolymers on the basis of Vinyl, acryl and Methacrylverbindungen, like z. B. Styrene, vinyltoluene, benzyle, phenyl, cyclohexyl acrylate and/or. - methacrylat in considerations. Suitable comonomers for these monomers to the other increase of the thermal stability are z. B. Allyl ester isomers of the benzene dicarbonic acids (1), trimellitic acid (2), Pyromellithsäure (3), Trimesinsäure (4) and the cyclohexanedicarboxylic acid (5), tri allyl cyanogen urate (TAC), tri allyl ISO cyanogen urate (TAIC) and the Diallylcarbonat of bisphenol A (DAB-A).

EMI3.1

Benzene dicarbonic acid allyl ester

R = allyl

EMI3.2

Trimellithsäureallylester

G 1 = H, allyl

R2 = H, allyl

R3 = allyl

EMI3.3

Pyromellithsäureallylester

G 1 = H, allyl

R2 = H, allyl

R3 = H, allyl

R4 = allyl

EMI3.4

Trimesinsäureallylester

G 1 = H, allyl

R2 = H, allyl

R3 = allyl

EMI3.5

Cyclohexane dicarbonic acid allyl ester

R = allyl

The radical polymerization of the monofunctional monomers made generally in solution in presence of Azobisisobutyronitril (AIBN) as initiator. In presence of cross-linkingable monomers it is meaningful to accomplish the radical polymerization in substance. The course of the radical polymerization can be pursued to refraktometrisch very good and can targeted stopped become, before the Galpunkt is achieved. The produced polymers are in organic solvents very good soluble. Preferred ones come solvents and/or. Solvent mixtures, like Methoxy-2-propylacetat, 2 - Heptanon, n-butyl acetate, Cyclohexanon and ethyl lactate to the application, which become also used in Resisten for the microlithography. The polymer content of the solutions used for coating is dependent of the desired layer thickness. Preferred ones become solutions with a polymer content of 5-25% used.

The stabilization of the spun on layers can become both in the oven and on the hot plate performed. The temperatures lie within the range of 80-160 DEG C. If the polymer systems contain cross-linkingable allyl groups, the temperature of the content of these groups, which can be selected, is dependent. The preferred temperature range is about 60-120 DEG C. The embossing conditions for the structure production, which can be selected, are dependent of many factors. At a embossing temperature of 80-100 DEG C over the glass transition temperature of the polymer and a pressure of 80-100 bar nano-structures with polymers generated can become, the 0-20 Gew. - % at polyfunctional allyl monomers contain. Opposite PMMA the structures possess a dual higher plasma corroding stability. The pattern definition of equidistant lines and bars is < /= 50 Nm. It is only limited by the resolution of the used stamp.

The cross-linking temperature of the allylgruppenhaltigen polymers is dependent of the composition of the polymers and lies above 120 DEG C. The crosslinking of the prepolymers can take place during the embossing process without other initiator addition. This is particularly the case if embossing temperatures up to 200 DEG C become selected. The cross-linking temperature leaves itself in addition, by initiators, preferably peroxides with

different thermal reactivity, like z. B. Benzoyl peroxide, the-t-butylperoxid and dicumyl peroxide, affect. The initiator concentration can lie between 2-7%. A thermal post treatment of the embossed structures is recommended if a particularly high thermal resistance and an high chemical resistance achieved to become to be supposed. It is also meaningful if the used prepolymers possess a low glass transition temperature and need therefore only a low temperature for coining/shaping. The embossing temperature should with an embossment of approx. are appropriate for 100 bar with 60-120 DEG C, preferred with 80-100 DEG C, over the glass transition temperature of the used polymer. Similar results become achieved with doped polymer solutions. The portion of caused allyl monomers is to preferred with 3-10 Gew. - %.

The subsequent examples are to describe the instant invention more near.

Examples

Example 1

Into a round bottom flask, provided with stirrer, thermometer, nitrogen introduction pipe and reflux condenser, 46 g Phenylmethacrylat, 95 become ml acetone and 46 mg Azoisobutyronitril (AIBN) given and 25 hours with 60 DEG C bottom agitation and nitrogen introduction polymerized. The approach become subsequent 30 ml acetone added, and the polymer becomes in 500 ml methanol over a dropping funnel precipitated and separated. The polymer becomes multiple dissolved and methanol precipitated in acetone. The separated polymer becomes anschliessend in the Vakuumtrockenschrank with 60 DEG C dried. The yield at Polyphenylmethacrylat amounts to 68% of the theory. The glass transition temperature of the polymer is about 125 DEG C.

Bottom comparable experimental conditions become subsequent polymers prepared:

Polymer	Glass transition temperature (DEG C)
Copolymer from Phenylmethacrylat and cyclohexyl methacrylate 60/40	106
Copolymer from Phenylmethacrylat and Benzylmethacrylat 60/40	91
Copolymer from Phenylmethacrylat and Benzylmethacrylat 40/60	79
Polybenzylmethacrylat	56
Polycyclohexylmethacrylat	93

Example 2

Into a round bottom flask, provided with stirrer, thermometer, nitrogen introduction pipe and reflux condenser, 200 g Phenylmethacrylat and 20 g diallyl phthalates and 440 mg AIBN become as initiator given and with 80 DEG C, 6 hours bottom nitrogen introduction polymerized. The polymerization process becomes refraktometrisch followed and short interrupted before the point of gel by cooling. 50 becomes ml acetone added. The precipitation of the prepolymer made in 800 ml methanol over a dropping funnel. The prepolymer is umgefällt separated and multiple by release in acetone and addition of methanol. The prepolymer becomes subsequent 6 hours with 40 DEG C in the Vakuumtrockenschrank dried.

Yield: 52% of the theory

Bottom comparable conditions become copolymers the subsequent composition prepared:

Copolymer	Gew. - %
Benzylmethacrylat/Diallylphthalat	80/20
Methylmethacrylat/Triallylisocyanurat	90/10
Styrene/Diallylphthalat	90/10

Example 3

With a 10%-igen solution of Polyphenylmethacrylat in Methoxypropylacetat becomes with a rotational speed of 3000 rpm an SI wafer coated. The coated wafer becomes subsequent 5 min with 140 DEG C on an hot plate thermally treated. The polymer film has a thickness of 290 Nm. The structure casting of 40 Nm structures of an embossing made at a embossing temperature of 200 DEG C and an embossment of 100 bar in an hydraulic press. The achieved structure casting corresponds to the structure of the stamp (1: 1-Abbildung of the structures, smallest resolution 40 Nm). For the structure casting comparable in examples 1 and 2 stated polymers result at embossing temperatures of 80-100 DEG C above the glass transition temperature of the polymers and an embossment of 100 bar. The casted structures become subsequent 5 minutes with 160 DEG C after-cured, without a flow of the structures is to be observed.

Example 4

With a 10%-igen solution of the copolymer Phenylmethacrylat/Diallylphthalat (90/10 Gew. - %) becomes in Propylenglykolmonomethyletheracetat (PGMEA) with a rotational speed of 3000 rpm. an SI wafer coated. Subsequent one becomes the coated wafer 5 min with 100 DEG C on an hot plate thermally treated. The polymer film has a thickness of 300 Nm. In an hydraulic press a structure becomes into the polymer film embossed with a stamp at a embossing temperature of 180 DEG C and a pressure of 100 bar. The structured wafers becomes after the cooling on 100 DEG C from the press taken. The casted structures become subsequent 5 minutes with 180

DEG C after-cured, without a flow of the structures is to be observed. It becomes a 1: 1-Strukturabformung achieved. In the CHF₃-Plasma at 1500 W a plasma corroding selectivity results opposite SiO₂ of > 2.

Comparable results become 2 obtained with the polymers in example.

Example 5

A 10%-igen solution from Polyphenylmethacrylat in Methoxypropylacetat 5 Gew become. - % diallyl phthalate (related to the polymer) and 5% the-t butylperoxid (related to the Diallylphthalatanteil) added. With a rotational speed of 3000 rpm a 3-Zoll-Si-Wafer becomes coated. Subsequent one becomes the coated wafer 5 min with 120 DEG C on an hot plate thermally treated. The polymer film has a thickness of 270 Nm. The structure casting of nano-structures of an embossing made in an hydraulic press at a embossing temperature of 180 DEG C and an embossment of 100 bar. The achieved structure casting corresponds to the structure of the stamp. One an achieved 1: 1-Strukturübertragung.

With a thermal post treatment 5 minutes with 160 DEG C no flow of the structures observed becomes.

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1. The invention relates to the application of materials for the Nanoimprintlithographie to the production of embossed nano-structures in thin layers on substrate documents, characterised in that of polymers with high plasma corroding stability and thermostability used will become, those at a embossing temperature of 60-180 DEG C, preferred with 80-100 DEG C over the glass transition temperature of the polymers embossed.

2. according to claim 1 characterised in that of polymers on the basis of aromatic and cyclo-aliphatic Vinyl, methacrylat and acrylate polymers and/or. their copolymers used become.

3. according to claim 1 characterised in that the materials polyfunctional allyl connections as monomer or as prepolymer added, their portion with a doping preferred become with 3-15 Gew. - % and with a copolymerization with 5-45 Gew. - is appropriate for %.

4. according to claim 1 characterised in that the embossing process so performed becomes that the cross-linking process of the allylgruppenhaltigen polymers takes place after made structure coinage in the pressing tool.

5. after. Claim 1 characterised in that the cross-linking process of the allylgruppenhaltigen polymers outside of the pressing tool by a thermal post treatment preferred in the temperature range of 140-200 DEG C made.

6. according to claim 3-5 characterised in that the polymers of peroxides in a concentration of 2-7% , related to the polymer content, added become.